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SILICON PRODUCTION PROCESS EVALUATIONS

QUARTERLY TECHNICAL PROGRESS REPORT (I)

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TREI
Texas Research and Engineering Institute, Inc.
6116 WASHINGTON
GROVES, TEXAS 77619

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DISCLAIMER

ABSTRACT

During this reporting period, chemical engineering analysis of the HSC process (Hemlock Semiconductor Corporation) for producing silicon from dichlorosilane was initiated.

For the preliminary process design, Hemlock Semiconductor Corporation was contacted in regard to providing a process flowsheet which best represents the HSC process at this point in time and which should be used for the chemical engineering analysis of a 1,000 MT/yr plant for solar cell grade silicon.

Major efforts in the chemical engineering analysis of the HSC process were devoted to the preliminary process design of a plant to produce 1,000 MT/yr of silicon using the technology. Progress and status for the plant design are reported for the primary activities of base case conditions (60%), reaction chemistry (50%), process flow diagram (35%), energy balance (10%), property data (10%), and equipment design (5%).

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I. CHEMICAL ENGINEERING ANALYSIS

Chemical engineering analysis of the HSC process (Hemlock Semiconductor Corporation) for silicon was initiated during this reporting period.

In performing the chemical engineering analysis, a process flowsheet is required for the preliminary process design. Hemlock Semiconductor Corporation has been contacted in regard to providing a process flowsheet which best represents the HSC process at this point in time and which should be used for the chemical engineering analysis of a 1,000 MT/yr plant for solar cell grade silicon.

The HSC process is based on the chemical vapor deposition of dichlorosilane (DCS) with hydrogen to produce polysilicon. This DCS deposition reaction rate is fast and has the following representative chemical reaction equation:

$$SiH_2Cl_2 + H_2 \rightarrow Si\downarrow + \text{By-products}$$

The above reaction equation may include several reaction steps. Chemical equilibrium is involved and in reality, several chlorosilanes (such as SiH_2Cl_2, $SiHCl_3$ and $SiCl_4$) are also present in the gas phase by-products.

For chemical engineering analysis of the HSC process, progress and status are summarized below for primary activities:

	Prior	Current
1. Base Case Conditions	0%	60%
2. Reaction Chemistry	0%	50%
3. Process Flow Diagram	0%	35%
4. Material Balance	0%	35%
5. Energy Balance	0%	10%
6. Property Data	0%	10%
7. Equipment Design	0%	5%

The detailed status sheet for the chemical engineering analysis is shown in Table I-1 for the preliminary process design of the plant. The base case conditions (issue 1) and reaction chemistry are given in Tables I-2 and I-3.

The process flow diagram (issue 1) is presented in Figure I-1. The conceptual-type process flowsheet in the figure shows the major unit operations involved in the production of the silicon product. The flowsheet, as shown, was prepared primarily from the 4th and 5th quarterly technical reports of Hemlock Semiconductor Corporation. Within this regard, Hemlock Semiconductor Corporation has been contacted again to provide an updated process flowsheet which best represents the HSC process at this point in time and which includes any process changes based on development work completed since the earlier quarterly technical reports.

Table I-1

CHEMICAL ENGINEERING ANALYSES:
PRELIMINARY PROCESS DESIGN ACTIVITIES FOR HSC PROCESS

Prel. Process Design Activity	Status	Prel. Process Design Activity	Status
1. Specify Base Case Conditions	◐	7. Equipment Design Calculations	◐
1. Plant Size	◐	1. Storage Vessels	◐
2. Product Specifics	◐	2. Unit Operations Equipment	◐
3. Additional Conditions	◐	3. Process Data (P, T, rate, etc.)	◐
		4. Additional	◐
2. Define Reaction Chemistry	◐		
1. Reactants, Products	◐	8. List of Major Process Equipment	O
2. Equilibrium	◐	1. Size	O
		2. Type	O
3. Process Flow Diagram	◐	3. Materials of Construction	O
1. Flow Sequence, Unit Operations	◐		
2. Process Conditions (T, P, etc.)	◐	8a. Major Technical Factors	O
3. Environmental	◐	(Potential Problem Areas)	O
4. Company Interaction (Technology Exchange)	◐	1. Materials Compatibility	O
		2. Process Conditions Limitations	O
4. Material Balance Calculations	◐	3. Additional	O
1. Raw Materials	◐		
2. Products	◐	9. Production Labor Requirements	O
3. By-Products	◐	1. Process Technology	O
		2. Production Volume	O
5. Energy Balance Calculations	◐		
1. Heating	◐	10. Forward for Economic Analysis	O
2. Cooling	◐		
3. Additional	◐		
6. Property Data	◐		
1. Physical	◐		
2. Thermodynamic	◐		
3. Additional	◐		

O Plan
◐ In Progress
● Complete

TABLE I-2

BASE CASE CONDITIONS FOR HSC PROCESS (ISSUE 1)

1. Plant Size
   - -Silicon produced from dichlorosilane (DCS)
   - -1000 metric tons/yr of silicon
   - -High purity silicon
   - -Final product form (solid rods)

2. Hydrogenation Reaction
   - -Metallurgical grade silicon, hydrogen, and recycle silicon tetrachloride (TET) used to produce trichlorosilane (TCS)
   - -Copper catalyzed
   - -Fluidized bed
   - -500°C, 514.7 psia
   - -29.5% conversion to TCS (example)

3. Recycle From Hydrogenation Unit
   - -Unreacted hydrogen from hydrogenation reactor is seperated from chlorosilanes by condensation and then recycled
   - -Unreacted silicon tetrachloride (TET) is seperated by distillation and recycled

4. Boron Removal
   - -Removal of BCl_3 by complexation with nitrogen or oxygen base chemical which is supported on non-volatile substance
   - -Fixed bed unit
   - -No chlorosilane material loss

5. TCS Redistribution Reaction
   - -TCS is redistributed to DCS and TET through catalytic reaction
   - -Catalytic redistribution of TCS with amine function ion exchange resin (Dowex Ion Exchange Resin MWA-1)
   - -Liquid phase 80 psia, 70°C
   - -Conversion from pure TCS feed is about 10.5% to DCS

6. Dichlorosilane Purification
   - -Final purification by distillation
   - -Designed to seperate DCS from TCS
   - -Overhead stream as the feed to CVD reactor
   - -Bottom stream as the feed to redistribution reactor

7. Chemical Vapor Deposition Reaction
   - -Silicon production
   - -Siemens CVD reactor (modified)
   - -Dichlorosilane and Hydrogen feed
   - -Molar conversion to silicon of 40%
   - -Deposition rate of 3000 g/hr
   - -Reactor exhaust gas composition (per mole of DCS fed)

HCl	.14
DCS	.10
TCS	.34
STC	.16

TABLE I-2 (CONTINUED)

8. Recycle From CVD Reactor
   - Chlororcilanes are recovered from a refrigeration process
   - Hydrogen is seperated from HCl by adsorption process and recycled back to the CVD reactor
   - Hydrogen chloride (HCl) is recovered as a salable by-product

9. Slim Rod Pullers
   - Prepare slim rods (small filaments)
   - Slim rods used in Siemen's CVD reactor for silicon deposition
   - Slim rod diameter of 6mm (approx. ¼ inch)

10. Operating Ratio
    - Approximately 85% utilization (on stream time)
    - Approximately 7445 hour/year production

11. Storage Consideration
    - Feed materials (several week supply, approx. 1 month)
    - Product (two shifts storage)
    - Process (several hours to 1 shift)

12. Wastes Treatment
    - Scrub and neutralize waste gas streams
    - Caustic solution used to neutralize

TABLE 1-3

REACTION CHEMISTRY FOR HSC PROCESS

1. Hydrochlorination Reaction

$$3SiCl_4 + Si + 2H_2 \rightleftarrows 4SiHCl_3$$

2. Redistribution Reaction

$$2SiHCl_3 \rightleftarrows SiH_2Cl_2 + SiCl_4$$

3. Waste Treatment (representative - overall)

$$SiH_2Cl_2 + Ca(OH)_2 \xrightarrow{aq.} SiO_2 + CaCl_2 + 2H_2O$$

$$SiHCl_3 + 1.5Ca(OH)_2 \xrightarrow{aq.} SiO_2 + 1.5CaCl_2 + 2H_2O$$

$$SiCl_4 + 2Ca(OH)_2 \xrightarrow{aq.} SiO_2 + 2CaCl_2 + 2H_2O$$

4. Decomposition Reaction

$$SiH_2Cl_2 + H_2 \rightarrow Si + \text{By-Products}$$

Note:

1. Reaction 1 product contains H_2, HCl, $SiCl_4$, $SiHCl_3$, SiH_2Cl_2 (trace), other trace chlorides
2. Reaction 2 product contains $SiHCl_3$, $SiCl_4$, SiH_2Cl_2, SiH_3Cl
3. By-products in reaction 4 include H_2, HCl, SiH_2Cl_2, $SiHCl_3$ and $SiCl_4$

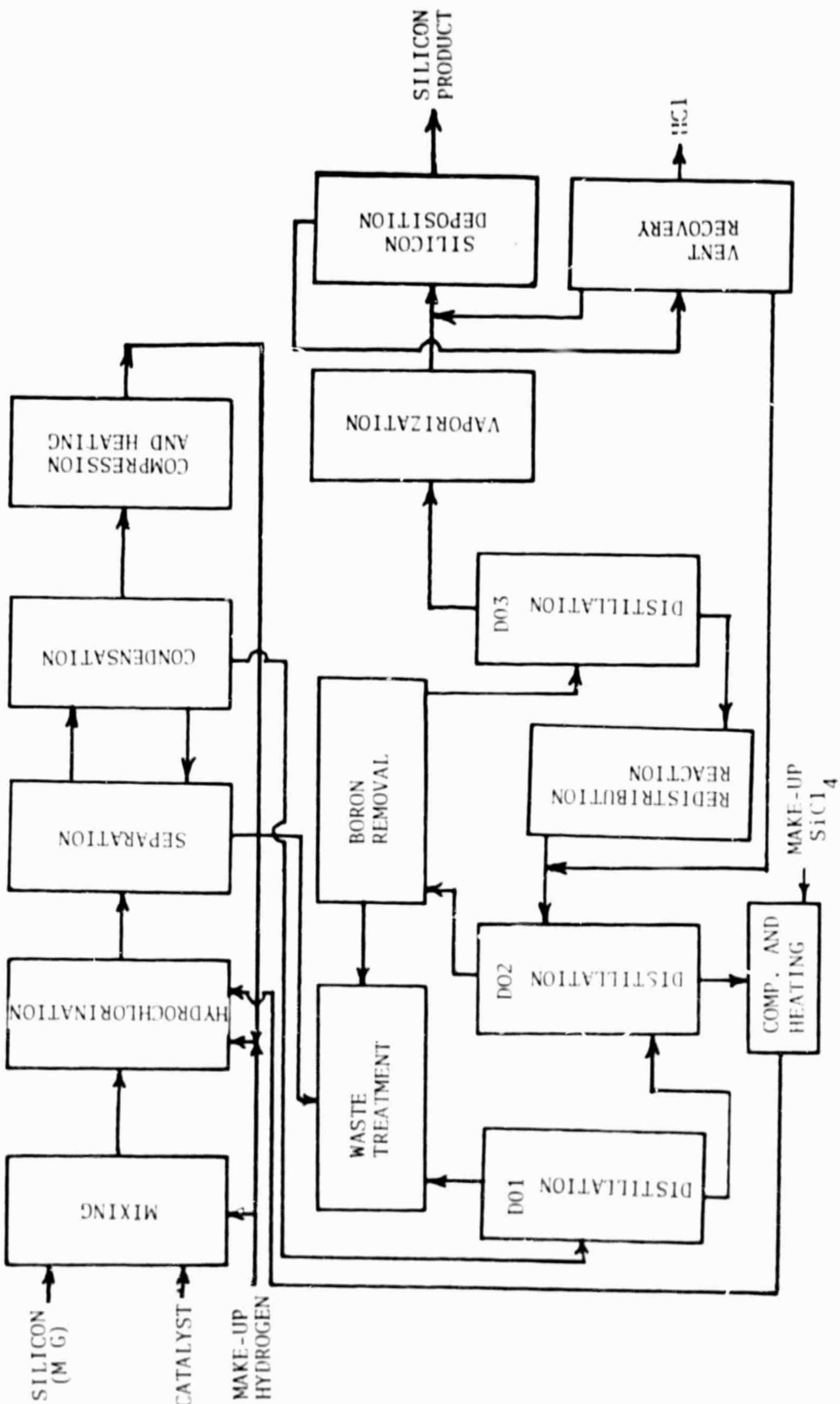

Figure I-1 Process Flowsheet for HSC Process (Issue 1)

II. SUMMARY - CONCLUSIONS

The following summary-conclusions are made as a result of achievements during this reporting period.

1. Chemical engineering analysis of the HSC process (Hemlock Semiconductor Corporation) for silicon was initiated.

2. Hemlock Semiconductor Corporation has been contacted in regards to providing a process flowsheet which should be used for the chemical engineering analysis of a 1,000 MT/yr silicon plant.

3. For chemical engineering analysis of the HSC process, major efforts were devoted to the preliminary process design of a plant to produce 1,000 MT/yr of silicon using the technology.

4. Progress and status are reported for the primary design activities of base case conditions (60%), reaction chemistry (50%), process flow diagram (35%), material balance (35%), energy balance (10%), property data (10%) and equipment design (5%).

III. PLANS

Plans for the next reporting period are summarized below:

1. Continue chemical engineering analysis of the HSC process (Hemlock Semiconductor Corporation) for silicon.

2. For the preliminary process design, major efforts will be devoted to:

   - base case conditions
   - reaction chemistry
   - process flow diagram
   - material balance
   - energy balance
   - equipment design

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